

Laboratory simulations of Mars evaporite geochemistry

Jeffrey M. Moore,¹ Mark A. Bullock,² Horton Newsom,³ and Melissa Nelson³

Received 30 May 2008; revised 1 September 2009; accepted 22 December 2009; published 22 June 2010.

[1] Evaporite-rich sedimentary deposits on Mars were formed under chemical conditions quite different from those on the Earth. Their unique chemistries record the chemical and aqueous conditions under which they were formed and possibly subsequent conditions to which they were subjected. We have produced evaporite salt mineral suites in the laboratory under two simulated Martian atmospheres: (1) present-day and (2) a model of an ancient Martian atmosphere rich in volcanic gases. The composition of these synthetic Mars evaporites depends on the atmospheres under which they were desiccated as well as the chemistries of their precursor brines. In this report, we describe a Mars analog evaporite laboratory apparatus and the experimental methods we used to produce and analyze the evaporite mineral suites. The acidic, “paleo-Mars” gas mixture was CO₂ with trace amounts of SO₂, N₂O, and HCl to simulate an atmosphere influenced by volcanic emissions. Brines formed by the interaction of water with an SNC-derived synthetic Mars mineral mix were produced under the acidic Mars atmospheric gas mixture. The brines were then desiccated under the two different simulated Mars conditions in the evaporite apparatus. Infrared reflectance spectroscopy and SEM microprobe analyses reveal that salts precipitated from the brine evaporated under simulated present Mars conditions were chemically different from those formed under the acidic Mars atmosphere conditions. The primary salt precipitated from the brine evaporated under present-day Mars conditions was a hydrated calcium sulfate, with lesser amounts of a magnesium sulfate and aluminum sulfate. Salts precipitated from the brine evaporated under an acidic atmosphere were dominated by magnesium sulfates, with lesser amounts of Na₂SO₄. These experiments suggest ways that relative cation abundances in Martian sulfate-bearing sediments can indicate the atmospheric and aqueous conditions under which they were formed. We conclude that the salts that make up the Meridiani sediments were probably formed by the interaction of water and igneous rocks at a high water-to-rock ratio, followed by desiccation under an atmosphere rich in acidic volcanic volatiles. The formation of Ca sulfates on Mars has most likely been due to the evaporation or freezing and sublimation of waters in equilibrium with an atmosphere much like the present.

Citation: Moore, J. M., M. A. Bullock, H. Newsom, and M. Nelson (2010), Laboratory simulations of Mars evaporite geochemistry, *J. Geophys. Res.*, 115, E06009, doi:10.1029/2008JE003208.

1. Introduction

[2] Evaporite mineralogy is apparently widespread on Mars. The stunning presentation of sulfate-rich sedimentary rocks that greeted the MER rover Opportunity when it first opened its eyes on Meridiani Terra leaves little doubt that liquid water was responsible [Squyres *et al.*, 2004]. The OMEGA visible and near-IR spectrometer on board the Mars Express spacecraft has detected large amounts of gypsum,

kieserite, and polyhydrated sulfates in Meridiani, Margaritifer, and the enclosed basins of the greater Valles Marineris region [Bibring *et al.*, 2005; Gendrin *et al.*, 2005]. CRISM on MRO found that layered deposits in the Valles Marineris exhibit stratification in sulfate and ferric mineral assemblages, suggesting a time-variable chemical environment [Murchie *et al.*, 2008]. In every case, sulfates are associated with light-toned layered deposits. Sulfates also exist in the large polar dune fields of Olympia Planitia [Langevin *et al.*, 2005; Murchie *et al.*, 2008]. Some layered sulfates, such as those exhumed at Meridiani Terra and in Juventae Chasma, are massive, with stacks up to 1 km thick or more [Bibring *et al.*, 2005; Gendrin *et al.*, 2005].

[3] In the case of Meridiani, and western Arabia in general, careful geological mapping of the light-toned sulfate-rich units that underlie the hematite regions detected by MGS TES [Christensen *et al.*, 2000a] reveals outliers with the same

¹NASA Ames Research Center, Moffett Field, California, USA.

²Department of Space Studies, Southwest Research Institute, Boulder, Colorado, USA.

³Institute of Meteoritics, Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, New Mexico, USA.

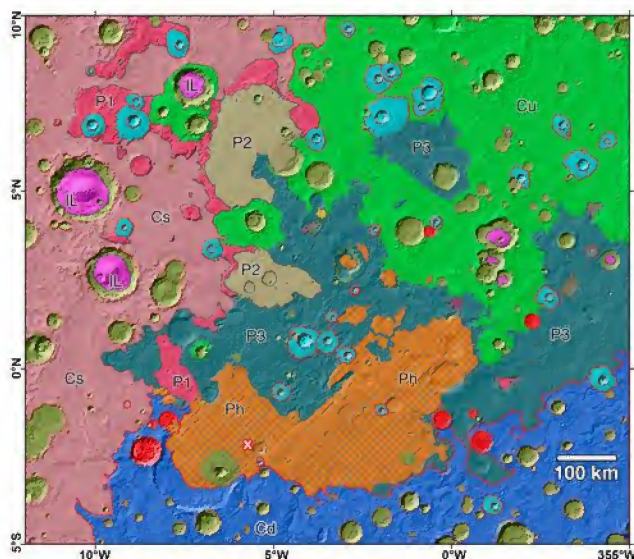


Figure 1. Geologic map of widespread differentially eroded sedimentary deposits of Meridiani Planum, which, in total extent, cover an area about the size of the Colorado Plateau and are collectively perhaps over 1 km thick. The various plains units (denoted by first letter P) are well layered and each up to ~200 m thick. Unit Ph is the gray hematite-bearing Meridiani Formation upon which MER B landed (white X marks location). Unit Cu is thought to be the highest stratigraphic unit by Hynek [2004], whereas both units Cu and Cd are considered by Edgett and Malin [2005] to be stratigraphically high. Both investigations place unit CS at the bottom of the stack, with layered unit IL just above it. Unit Cd is also thought by Hynek [2004] to be low. Small outcrops of crater material are unlabeled. Map modified from Hynek *et al.* [2002], courtesy of B. Hynek.

sedimentary sequence, implying that the thick stack of sulfates covers tens of thousands of square km [Griffes *et al.*, 2007; Poulet *et al.*, 2008]. Geologic mapping of Meridiani hematite units shows that they are in the midst of at least a 600 m thick stack of friable layers superposed on middle to late Noachian cratered terrain [Christensen and Ruff, 2004; Edgett and Malin, 2002, 2005; Hynek *et al.*, 2002]. Bedding remains consistent and uniform over thousands of square km. In places, erosion has removed vast portions of the stratigraphic sequence (Figure 1). The implication is that this entire region, about the size of the Colorado plateau, was inundated with water episodically, buried, and then exhumed [Edgett and Malin, 2002, 2005; Hynek, 2004]. A similar stratigraphic sequence is observed in the plains cut by some parts of the Valles Marineris. Looking at sequences in NW Meridiani and SW Arabia Terra, Edgett and Malin [2005] concluded that they are just a small part of a regional occurrence of light-toned sedimentary rocks that outcrop all across Meridiani and underlay the hematite layer. In some areas, as much as 600 m has eroded away, exhuming deeper underlying layers.

[4] In addition to sulfate-rich layers, deposits that contain clays have been observed by OMEGA in the Mawrth Vallis region of Arabia, as well as elsewhere [Loizeau *et al.*, 2007; Poulet *et al.*, 2005]. This led Bibring *et al.* [2006] to propose

that Mars has had three different epochs of aqueous history: The first, during the early and mid-Noachian was characterized by a vigorous hydrologic cycle, near neutral pH waters, and the alteration of basalts to phyllosilicates. The next chemical epoch was characterized by smaller amounts of sulfuric acid-laden waters and the deposition of sulfates during the late Noachian to mid-Hesperian. From just before the Amazonian on up to the present, the surface has been superficially weathered with almost no liquid water, producing the ubiquitous anhydrous ferric oxides.

[5] The horizontal extent and continuity of the Meridiani layers is consistent with their being laid down as lacustrine or marine deposits. MER Opportunity has shown locally that even aeolian sandstone can harbor sulfate cement, presumably emplaced by groundwater [McLennan *et al.*, 2005]. Analysis of the geomorphic and bedding features of outcrops in Eagle, Endurance, and Erebus craters, such as cross lamination and the festoon features seen at cm scales also indicates that these rocks, at least, were laid down in a shallow body of water that experienced flow rates of tens of cm/s [Grotzinger *et al.*, 2006, 2005; Squyres *et al.*, 2004]. Other interpretations exist. It has been suggested that the morphological features seen at small scale attest to their production by an impact [Burt *et al.*, 2005] or as altered pyroclastic deposits [Arvidson *et al.*, 2003; Hynek *et al.*, 2002]. Sulfate cements within aeolian sandstone are consistent with the idea that circulating fluids at depth could have also been responsible for the formation of the hematite seen at Meridiani [Christensen and Ruff, 2004; McLennan *et al.*, 2005].

[6] The existence of massive layers of sulfates on Mars is a tremendous clue to its ancient aqueous and climate history [Bibring *et al.*, 2006; Bullock and Moore, 2007; Moore, 2004]. The chemical and physical nature of these deposits record the conditions under which they were formed, altered, and later revealed by erosion. In order to connect these exciting discoveries on Mars to their meaning for the history of the planet, it is essential to understand how sulfates and other salts are formed under Martian conditions.

2. Sedimentary Rocks at Meridiani Planum

[7] Sedimentary rocks at Meridiani are made up of fine-grained particles, Mg and Fe sulfates, and spherule concretions of hematite. The sulfates make up to 40% of the mass of the outcrop, while jarosite, $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ makes up about 8% of the sulfates [Clark *et al.*, 2005]. Hematite makes up about 10% of the mass of the outcrops. S is enriched in outcrops compared to soil, but Cl is not. This suggests fractionation by differential solubility. Br, however is highly variable over short length scales. Since bromides are more soluble than chlorides for the same cation, the variation is clearly due to differential solubility and transport by water. Most of the salts are hydrated, providing some of the H signature seen by the Mars Odyssey Gamma Ray Spectrometer [Arvidson *et al.*, 2005]. The sediments have had a complex history of diagenesis, with the formation of spherical hematite concretions 4–6 mm in diameter and crystal mold vugs. The tabular shape of the vugs ($1\text{--}2 \times 10$ mm) is consistent with their being formed by crystals of gypsum or Mg sulfate, which were then later dissolved by water and removed. Linear deconvolution of Mini-TES spectra of Meridiani outcrops shows them to be composed primarily of amorphous silica/

glass/phylosilicates and Mg-, Ca-, and Fe-bearing sulfates, and smaller amounts of plagioclase [Glotch and Bandfield, 2006].

3. Theories of the Origin and Evolution of the Martian Salts

[8] The sulfates of Mars are the remains from epochs of more vigorous hydrology and erosion. They are possibly the detritus of a lost ocean or the stored products of globally extensive rock/volcanic acid interactions in the post Noachian [Banin *et al.*, 1997]. Alternatively, the Martian soil may largely be the products of high-temperature aqueous alteration, derived from volcanic or impact hydrothermal systems [Newsom and Hagerty, 1997]. Proposed explanations for the origin of mobile ions in the Martian soil fall into four categories: (1) high-temperature hydrothermal alteration of basalts, (2) deposition by volcanic aerosols and gases, (3) groundwater interactions with igneous rocks, and (4) contributions from meteoric infall. The dominance of one or more of these processes can be distinguished in principle by observing bulk and trace element enrichment patterns and mineralogy. Each process has important implications for the nature and history of water on Mars.

[9] Clark and Van Hart [1981] pointed out that the Martian salts could have formed by either chemical weathering of igneous rocks due to liquid water [Clark *et al.*, 1976; Toulmin *et al.*, 1977] or by gases released during volcanic activity, fumarole venting, or surfaceward migration of gases from magma chambers. Newsom and Hagerty [1997] proposed that the globally ubiquitous, homogeneous fines units on Mars are composed of some mixture of three types of basaltic alteration products: Those produced by volcanic and impact degassing, hydrothermal processes, and chondritic material. Banin *et al.* [1997] performed experiments involving the acidification of partly palagonitized tephra in order to assess the possibility that mobile components in the Martian soil are enriched due to geologically recent interaction of volcanic acidic volatiles with basalts. They noted that the formation of nanocrystalline iron oxide phases that seem to characterize much of the Martian fines materials are inconsistent with the dry conditions that prevail today. They suggested instead that the topsoil layers of Mars may have been formed by extremely slow, ongoing weathering interactions, driven by acidic volatiles deposited from the atmosphere in the recent, dry environment of Mars.

[10] McSween and Keil [2000] deduced the composition of the pervasive global dust layer of Mars by plotting various mixing trends of oxides and SO₃ from Viking and Pathfinder elemental analyses. Chemical compositions of soils at Viking 1 and Mars Pathfinder landing sites show different effects of mixing. Viking soils contain varying amounts of chloride and sulfate salts as cements, while compositional variations in the Pathfinder APXS data result from admixture of small fragments of local andesitic rock. The two mixing trends intersect at approximately the same composition, which probably represents a globally homogeneous dust. This composition lies along weathering trends for terrestrial basaltic rocks, rather than andesitic or other felsic lithologies. They concluded that the basaltic protolith was chemically similar to the basalts found in the shergottite meteorites. They suggested that palagonitization, rather than hydrothermal alteration at higher

temperatures or reactions with acidic volcanic volatiles, may be the best analogy for the formation of the Martian soils.

[11] Zolotov and Shock [2005] hypothesized that regional heating at Meridiani caused a release of sulfide-rich water. They calculated that near-surface aqueous oxidation of pyrite could lead to the sulfate chemistry seen in Meridiani by MER Opportunity. In laboratory experiments, Chevrier *et al.* [2004] were able to replicate some of the inferred Meridiani sulfate mineralogy by the weathering of iron, magnetite, and pyrrhotite under simulated Martian conditions. Detailed experiments on the nature of evaporites produced in simulated Martian conditions show that basalt aqueous weathering leads to Mg-Fe-SO₄-Cl brines depleted in Ca, Al, and K [Tosca and McLennan, 2006]. Modeling and laboratory analyses [McLennan *et al.*, 2007; Tosca *et al.*, 2005, 2008] suggest that the aqueous weathering of olivine-rich basalts in acidic conditions predicts many of the features of the sulfate and iron phases seen at Meridiani.

4. Experimental Apparatus

[12] Laboratory experiments were conducted to determine the identity of evaporites that would result from the dehydration of the brines produced in our earlier experiments. Our goal was to form these evaporites under controlled Mars-like conditions. To accomplish this, we designed and fabricated the Mars evaporites experimental apparatus. The Mars evaporites experimental apparatus has been carefully designed to provide a Mars-like environment with finely controlled pressure, temperature, gas flow, gas composition, and liquid environments for up to nine independent reaction vessels. Care was taken to design and fabricate a robust experimental apparatus that maintains sample and reaction vessel integrity. The Mars evaporites experimental apparatus consists for five major subsystems, which work together to maintain the precise environmental conditions (Figure 2). The five subsystems of the apparatus are (1) the sample vessel container block; which sits within (2) the hermetically sealed environment chamber; (3) a closed-loop vessel container block temperature control system; (4) a closed-loop environment chamber pressure and gas flow system; and (5) a computer-controlled temperature, pressure, and O₂ sensor data logger.

[13] A laptop computer running Labview, with a PCMCIA data acquisition card serves as the controller and logger, measuring temperature and pressure in the chamber, logging data and controlling the gas pressure in the chamber. All of these subsystems create and maintain the integrity of an isolated Mars environment-simulating system with nine sample locations for evaporite aliquots.

4.1. Sample Vessel Container Block

[14] The sample vessels are supported within an 18 × 16 × 10 cm stainless steel block which was machined to accept cylindrical sample receivers and coolant fluid. Formation of the evaporites is carried out in thin, conical 50 cc Teflon sample holders that sit inside and line the cylindrical receivers. Precipitation occurs at the bottom of each sample holder on a gold-plated TEM sample grid with a holey carbon thin film, which is removed at the conclusion of a run and sent to a lab for analysis. Each receiver contains a conical cavity for supporting the Teflon sample holders, a helical groove about the outside diameter, and two O rings to contain

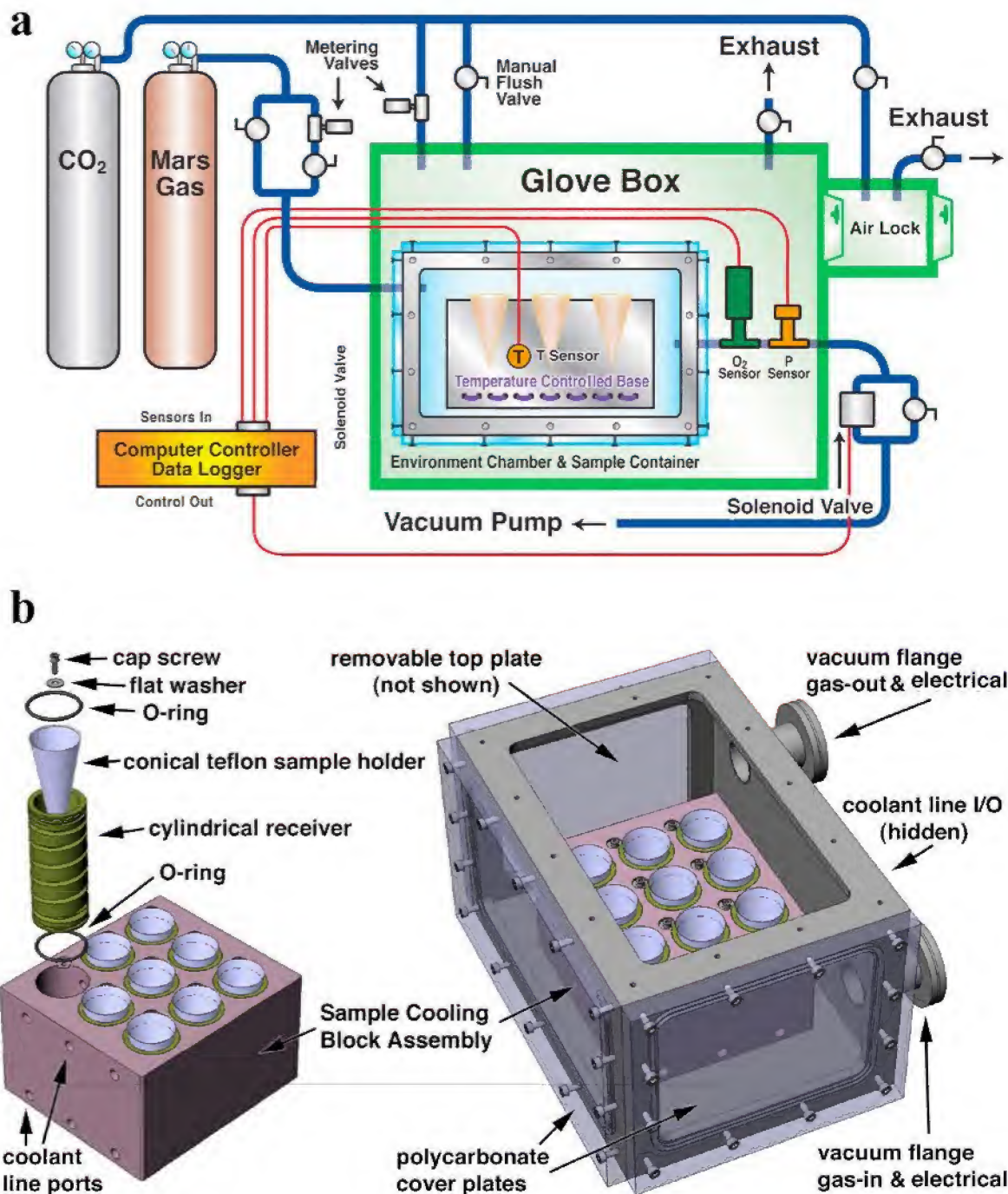


Figure 2. Schematic diagrams of the Mars evaporites experimental apparatus. (a) The environmental chamber encloses the sample vessel container block. Computer-controlled closed-loop circuits maintain pressure and temperature within the environment chamber. An O₂ sensor monitors the system for contamination. (b) Nine conical Teflon sample holders sit within cylindrical receivers outfitted with helical grooves through which a coolant is circulated for maintaining a constant temperature. The Plexiglas and steel environment chamber has gas, coolant, and electrical feedthroughs.

coolant. The helical groove provides efficient circulation of the coolant near each sample for temperature stability. The sample holders and receivers are mounted into the stainless steel block that is itself fitted with coolant lines to further ensure an isothermal environment. Temperature sensors are also distributed within the block.

4.2. Environment Chamber

[15] The entire sample vessel container block resides within an environment chamber with interior dimensions of $33.5 \times 21 \times 18$ cm. The environment chamber is composed of Plexiglas walls hermetically affixed to a stainless steel frame

and able to maintain a pressure as low as 10 mbar against ambient pressure with a leak rate of up to 0.1 mbar/s at 10 mbar. The top-facing Plexiglas wall is easily detached to allow access to the sample face of the sample vessel container block. The widespread use of Plexiglas, stainless steel, and Teflon throughout the apparatus is so that corrosive gases can

be used without fear of reaction that could either change the chemical evolution of the samples or jeopardize the integrity of the apparatus (Figure 3).

[16] The environment chamber itself resides within a $85 \times 59.5 \times 50$ cm Plexiglas glove box, which is slightly overpressurized with CO_2 for the duration of an experiment, and can be flushed with CO_2 while samples are being setup or extracted. Samples can be moved in and out of the glove box through an air lock, which can also be flushed with CO_2 . The slight overpressurization of the glove box serves as an additional barrier to O_2 contamination from any small leaks of the underpressurized environment chamber.

4.3. Temperature Control System

[17] The temperature of the samples is controlled by their placement deep within the sample vessel container block. The sample vessel container block has a large thermal mass in order to minimize temperature fluctuations in the samples. The sample vessel container block's temperature is controlled by a liquid recirculating temperature control unit (TCU), which receives temperature information from several thermistors embedded within it. The TCU uses ethylene glycol as the recirculating fluid. The fluid circulates within the aluminum block via channels machined into it that transmit coolant to each cylindrical sample receiver, whose exterior helical grooves provide a circuit for coolant around each receiver. This closed-loop temperature control system keeps the pallets and sample flasks within $\pm 1.0^\circ\text{C}$ of the designated set point (between -40°C and 25°C) for the duration of the experiment.

4.4. Gas Flow System

[18] The environment chamber has been fitted with two gas valves: one for flushing its interior with a synthesized Mars gas and the other for providing the environment chamber with gas (and water vapor) outflow and maintaining a constant pressure. The chamber can be maintained at any pressure between 1 and 1000 mbar with 1 mbar accuracy. The gas input and output valves are Teflon solenoids, which can be actuated both manually and by the computer controller. In line with the input valve is a metering valve so that the rate of input can be finely adjusted. The environment chamber pressure is measured every second, while the mean pressure is logged every 60 s. The pressure reading is used by the computer to regulate the environment chamber pressure. Every 5 s the computer averages the last five measurements from the pressure sensor. The average is taken to remove the effect of minor fluctuations in the pressure that might be

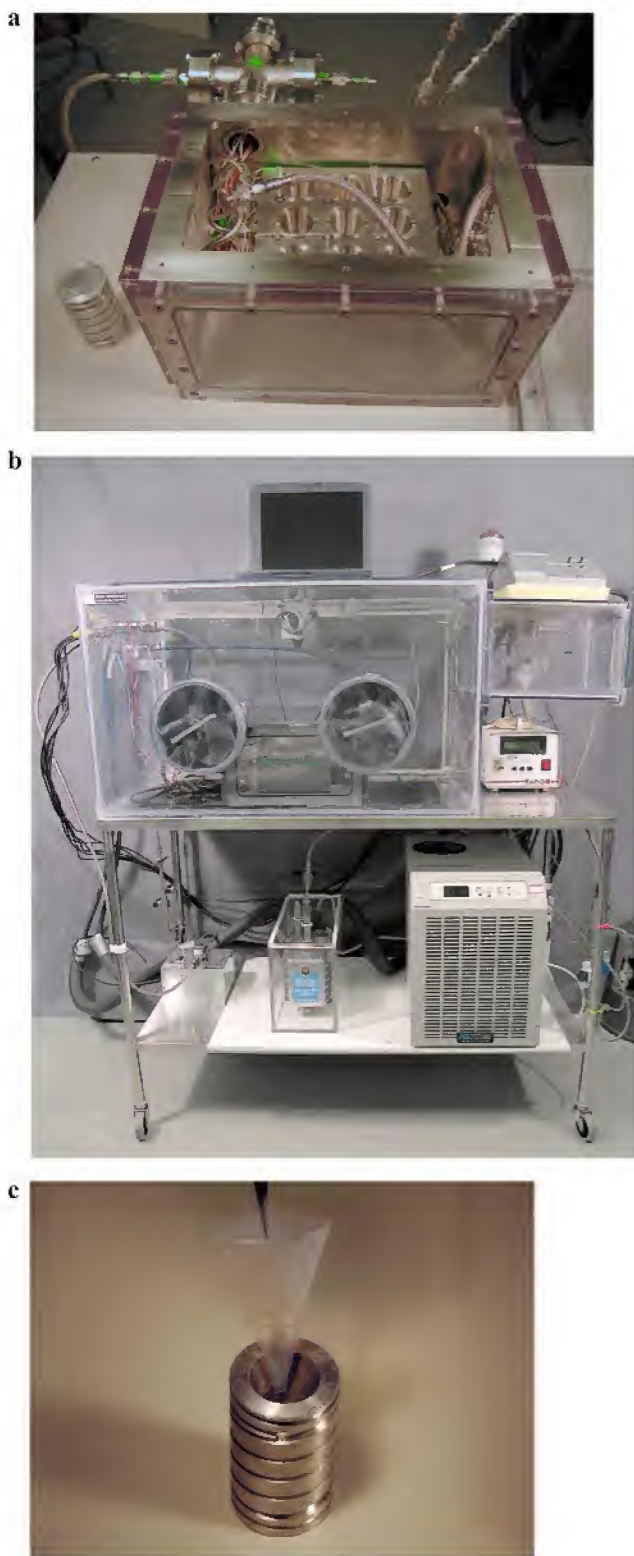


Figure 3. (a) Environment chamber with interior sample vessel container block. Gas and electric feedthrough can be seen at the rear of the chamber. On the far left is one of nine cylindrical sample receivers, with helical grooves for circulating coolant. (b) Entire Mars evaporite experimental apparatus. The environment chamber sits within the Plexiglas glove box. Above the glove box is the controller computer running Labview. To the right of the glove box is the air lock, with some interface electronics on top of it. Below the glove box are additional electronics and the recirculating heater/cooler. (c) Conical Teflon sleeve in which the precipitates form, and cylindrical sample receiver with helical coolant grooves.

Table 1. Synthetic Mars Analog Brines Recipe for an Acidic Mars Paleatmosphere

	Ion	K	Fe	Al	Mg	Ca	Na	Cl	NO ₃	SO ₄	CO ₃	Si
Salt	[M]	1.79E-05	5.37E-07	3.45E-04	2.01E-03	1.42E-03	1.44E-04	5.36E-05	8.06E-06	2.45E-04		7.80E-04
KCl	1.79E-05	1.79E-05						1.79E-05				
FeCl ₂	5.37E-07		5.37E-07					1.07E-06				
Al ₂ (SO ₄) ₃	8.15E-05			1.63E-04						2.45E-04		
Al ₂ (CO ₃) ₃	9.08E-05			1.82E-04							2.72E-04	
MgNO ₃	8.06E-06								8.06E-06			
MgCO ₃	2.01E-03				2.01E-03						2.01E-03	
Na ₂ CO ₃	7.18E-05						1.44E-04				7.18E-05	
CaCO ₃	1.42E-03					1.42E-03					1.42E-03	
HCl	3.46E-05							3.46E-05				
Remainder		0.E+00	0.E + 00	1.E-15	0.E + 00	0.E + 00	0.E + 00	0.E + 00	0.E + 00	0.E + 00		

caused by an immediately proceeding pressure adjustment. If the environment chamber pressure rises by more than 1 mbar of the preset pressure, the computer responds by opening a solenoid valve for 1 s and allowing access to a continuously operating vacuum roughing pump to depressurize the system. If the environment chamber pressure is within its preset value, the system is not depressurized and the computer continues in its “measure and check” cycle.

4.5. Temperature, Pressure, and O₂ Data Logging

[19] A Cambridge Sensotec Rapidox 200 O₂ sensor (capable of detection of O₂ down to 10–17 ppm) has been fitted into the output line. O₂ is constantly monitored by the computer controller in order to detect any oxygen contamination. An electrical feedthrough allows signals from thermistors attached to the sample vessel container block to be passed to the computer logger/controller.

5. Experimental Procedures

5.1. Synthetic Brines Formulation

[20] The production and analyses of Mars analog brines under present-day Mars conditions [Bullock *et al.*, 2004] and under a more acidic, paleo-Mars atmosphere [Bullock and Moore, 2004] supplied us with the possible ionic contents of subsurface waters on Mars. We found that cation and S/Cl ratios in laboratory brines produced under present-day Mars conditions were similar to those of the Martian fines measured at the two Viking lander sites and at the Mars Pathfinder landing site. However, brines produced in our laboratory under a gas mixture with SO₂, NO₂, and HCl had enhanced Ca and Mg abundances and a S/Cl ratio about 2 orders of magnitude higher than the Martian fines. These latter brines may be more representative of waters that hosted the precipitation of some sulfates on Mars [e.g., Zent and Fanale, 1986; Zent *et al.*, 1990], such as those seen at Meridiani, since the ancient Meridiani outcrops are many times higher in sulfate than the globally homogeneous fines. The evaporites we report on here were produced from synthetic versions of these brines. Because laboratory brine formation takes about a year under simulated Mars conditions and yields only a small amount of brine, we used the cation and anion analysis of these brines [Bullock and Moore, 2004] to create a recipe for identical synthetic brines. It is these that were used to create Mars analog evaporites.

[21] The reaction equations and equilibrium concentration modules of Outokumpu HSC chemistry software were used

to calculate equilibrium constants at 3°C and to determine the type and quantity of salts used to prepare the solution. Reagent grade salts (Aldrich chemical) were used in a combination that allowed the desired concentrations of ions to remain in solution without causing precipitation due to common ion effects. The first step of the preparation procedure involved dissolution of the calcium carbonate component of the brine using an acidic silica standard solution. Once the carbonate dissolved, this solution was diluted using 18 mOhm ultrahigh purity water (Milli-Q) to create a 21 ppm silica solution. The other salts were then sequentially dissolved in this solution, which contained the desired quantity of dissolved silica. Table 1 shows the salt concentrations used to make the synthetic brine. The second row lists the ion concentrations of the experimental brine, while the second column shows the concentration of salt used in the synthetic brine. The last row shows the difference in concentration between the experimental and the synthetic brines.

5.2. Laboratory Procedures

[22] The initial experiment was a study of evaporites formed by rapid evaporation of the synthetic brine formed under modern Mars conditions. We conducted an analysis of our synthetic brine and compared its composition with the brine produced in our brine experiment. We found that the synthetically produced brine was quite similar to that created in our yearlong experiment, except that the synthetically produced brine (SPB) was higher in sulfates by about an order of magnitude (Figure 4). The SPB was created using deoxygenized water. The stored SPB was sealed (with an argon headspace) to prevent the reintroduction of oxygen. Prior to the drawing of aliquots, the SPB was aerated with argon for 12 h. SPB, thus prepared, was passed into the Plexiglas glove box, which was overpressurized with argon as well.

[23] The necessary tools to draw and measure aliquots of SPB were already present within the glove box. Aliquots of the SPB were placed into nine sample holders (in the amounts of 3 at 20 ml, 3 at 10 ml, 3 at 5 ml). The filled sample holders were then placed into their individual sample receivers. The sample chamber (within the glove box) was then sealed and the Mars Gas Simulant (MGS) was introduced into the sample chamber. The sample chamber was first cooled to the experiment-run operating temperature (see Table 2). Then the pressure within the sample chamber was slowly adjusted to the experiment-run operating pressure (Table 2). Pressure, gas flow rate, MGS composition, and temperature were held

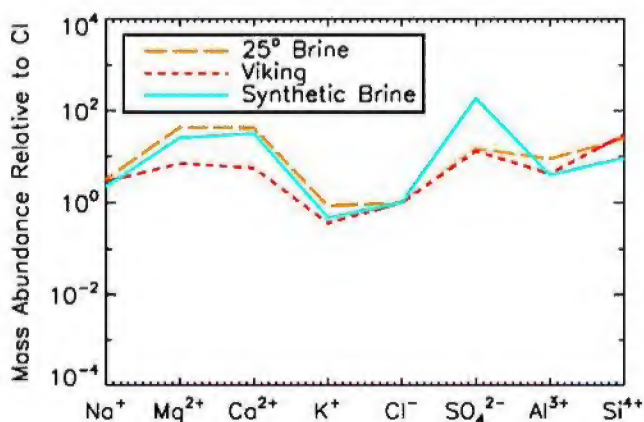


Figure 4. Composition of synthetic brine used to create evaporites (solid light blue line) compared with the composition of brine produced in the experiments reported by *Bullock and Moore* [2004] (long-dashed orange line) and the average composition of Viking soils (dashed red line).

constant throughout the experiment. Argon was used to maintain positive pressure within the glove box throughout the experiment as a means of preventing sample chamber gas contamination. Video cameras provided supervision of the evaporation process. Visual desiccation progress was logged. Pressure, temperature, and the absences of oxygen contamination were automatically logged throughout the experiment.

[24] When the samples were observed to be thoroughly desiccated, the pressure and temperature of the sample chamber were brought to ambient, but with the continued flow of MGS within in the sample chamber. The glove box was then purged for 24 h with the experiment-specific MGS. Once this was done, the sample chamber was unsealed (still under MGS purge within the glove box) and the sample-containing sample holders were immediately removed, sealed and passed out of the glove box. Samples were then prepared for overnight transportation for analysis (Figure 5).

5.3. Salt Production via Fast and Slow Evaporation

[25] Brines formed in the subsurface of Mars during periods rich in sulfur gases due to volcanic activity may have evaporated during the same era or may not have evaporated until later in the colder, drier climate that characterizes the Amazonian. Synthetic brines were made from the chemistry of water derived from incubating a Mars analog mineral mix in water under an acidic Mars analog paleoatmosphere [Bullock and Moore, 2004]. We then synthesized two kinds of evaporites: those formed by the evaporation of brines under simulated present-day conditions and those formed by the evaporation of brines under an acidic atmosphere with 100 ppm SO_2 , 10 ppm NO_2 , and 10 ppm HCl .

Table 2. Experimental Matrix for Mars Evaporites Production

Evaporation Style	Conditions	Modern Mars Gas	Paleo-Mars Gas
Fast	T = 25°C, 50 mbar	1–9	19–27
Slow	T = 0°C, 10 mbar	10–18	28–36

[26] Each type of evaporite was subjected to two modes of desiccation: fast at 25°C and 50 mbar and slow at 0°C and 10 mbar. For each of these four experiments, the synthetic brines were placed into nine sample holders (in the amounts of 20 ml) and desiccated under simulated Mars atmospheres under conditions listed in the experimental matrix (Table 2). Nine aliquots each were desiccated by fast (days) and slow (weeks) evaporation, and under the flow of a Mars analog present atmosphere and an acidic Mars analog paleoatmosphere. The aliquot numbers for each of the experiments are listed in Table 2.

6. Evaporite Analyses and Results

6.1. Infrared Spectroscopic Analysis

[27] In order to compare our synthetic evaporites with those found at the surface of Mars, we obtained infrared reflectance spectra of each of our samples. Samples were shipped to the Planetary Electrical Properties and Geochemistry (PEPG) laboratory at Southwest Research Institute in Boulder, Colorado. We used a Thermo Electron 6700 Fourier Transfer Infrared Spectrometer (FTIR) with an ETC Everglow mid-infrared source, KBr beam splitter, and MGTS detector. The spectrometer was fitted with a diffuse reflectance attachment for obtaining measurements most comparable to remotely sensed IR spectra at Mars from MiniTES. Spectra were obtained for each evaporite suite from 4000 to 500 cm^{-1} (2.5 to 20 μm) at a resolution of 1 cm^{-1} . For purposes of comparison, we obtained spectra under identical conditions for gypsum, kieserite, and copiapite. Figure 6 (top) is a reflectance spectrum for sample C, the precipitate produced during evaporation under the modern Mars gas mixture. Sample C consisted mostly of blades of crystals, sometime in contact with a more amorphous precipitate. Below the sample C spectrum are the comparison spectra. Features common to both kieserite and gypsum are seen in the sample C spectrum.



Figure 5. Salt precipitates produced in the Mars evaporites apparatus. Approximately 50 mg of evaporites were formed from 20 ml of brine. Salts were sealed in the conical Teflon sleeves by folding and taping the wide end. The sealed sleeves were then shipped to the Planetary Electrical Properties and Geophysics Laboratory at Southwest Research in Boulder, Colorado, for infrared spectral analysis, and to the Institute for Meteoritics at the University of New Mexico for SEM and microprobe analysis.

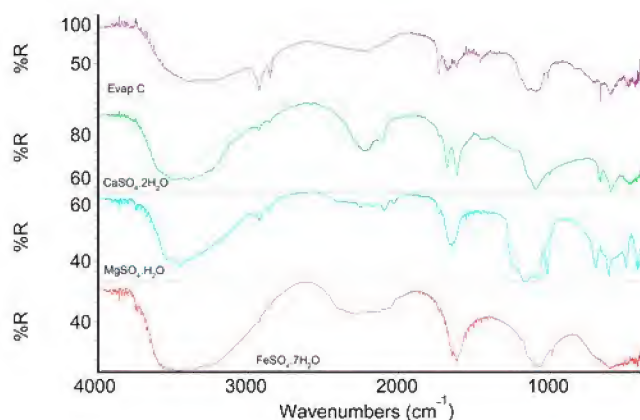


Figure 6. FTIR reflectance spectrum of evaporite formed by fast evaporation of Mars analog brine under simulated acidic conditions on Mars. The broad dip at 3500 cm^{-1} is diagnostic of sulfates, but the depth of the double band at 3000 and 3100 cm^{-1} and the structure of the $900\text{--}1200\text{ cm}^{-1}$ region is indicative of kieserite. The structure from 1500 to 1700 cm^{-1} , however, is much more consistent with gypsum. Comparison with the ASU spectral library [Christensen *et al.*, 2000b] shows the presence of Ca and Mg sulfates. Spectra of gypsum, kieserite, and ferrous sulfate, taken with the same instrument under the same conditions are shown for comparison.

For identification of spectral features, we employed the Arizona State spectral libraries [Christensen *et al.*, 2000b]. The broad dip at 3500 cm^{-1} is diagnostic of sulfates, but the depth of the double band at 3000 and 3100 cm^{-1} and the structure of the $900\text{--}1200\text{ cm}^{-1}$ region is indicative of kieserite. The structure from 1500 to 1700 cm^{-1} , however, is much more consistent with gypsum. The infrared spectrum sample C, the precipitate formed by evaporating brine under current Mars conditions, indicates that it is mostly composed of a mixture of gypsum and kieserite.

[28] Precipitates from the evaporation of Mars analog brine under an acidic atmosphere, labeled sample F, had a more fluffy, amorphous appearance in the microscope with smaller amounts of long crystals. The infrared reflectance spectrum of this precipitate is shown below in Figure 7. The same comparison spectra for kieserite, gypsum, and copiapite are also shown. Sample F has the diagnostic deep bands at 3000 and 3100 cm^{-1} of a CaSO_4 , probably kieserite, although more hydrated forms are also possible. The deep band at 1700 cm^{-1} indicates that other phases are present, although comparisons with all the available spectra for salts from the ASU SpecLab library yielded no plausible candidates.

6.2. SEM Imaging and Microprobe Analysis

[29] Evaporite samples were shipped to the Institute of Meteoritics at the University of New Mexico for SEM imaging and microprobe elemental composition analysis. Analyses for both sets of experiments were conducted at the University of New Mexico using a JEOL SEM and JEOL 8200 electron microprobe. Backscattered electron images were obtained using the Institute of Meteoritics JEOL 5800LV scanning electron microscope (SEM) with an attached

Oxford Isis Series 300 energy dispersive microanalytical system. The SEM was optimized for high-resolution imaging, which requires a 20 kV acceleration voltage, a sample current of 20 nA , a spot size of $8\text{--}10\text{ nm}$, and a working distance of $8\text{--}16\text{ mm}$.

[30] Elemental compositions and electron micrographs of five precipitate samples are shown in Figure 8. Below each micrograph is a plot of the elemental composition of the evaporite (blue solid lines) compared with the elemental composition of Mars' global fines from Viking Lander XRF data (red dashed lines). Evaporites formed by evaporation under simulated present-day Mars atmosphere are shown in the first three columns. The blade-like crystals precipitated under these conditions are mostly calcium sulfate, and the elemental compositions are dominated by Ca and S. However, small amounts of Al are found in the precipitate samples of the second and third columns, and some Mg appears in the precipitate shown in the third column. Mass balance strongly suggests that in addition to the dominant CaSO_4 , smaller amounts of MgSO_4 and $\text{Al}_2(\text{SO}_4)_3$ (alunagen) also precipitated when the S-rich brine was evaporated under modern Mars conditions. In contrast, brines that were evaporated under a simulated Mars atmosphere rich in acidic gases produced precipitates that were more blob-like in the electron micrographs. Elemental analysis of these samples, in the fourth and fifth columns of Figure 8, show that they are dominated by magnesium sulfates. A small amount of Na appears in the elemental analysis of the precipitate in the fifth column. Once again, mass balance argues that this is probably precipitated Na_2SO_4 , as either thernardite or mirabilite.

7. Discussion

[31] The Mars analog brines that evaporated into a paleo-Mars, acid-rich atmosphere produced precipitates slightly

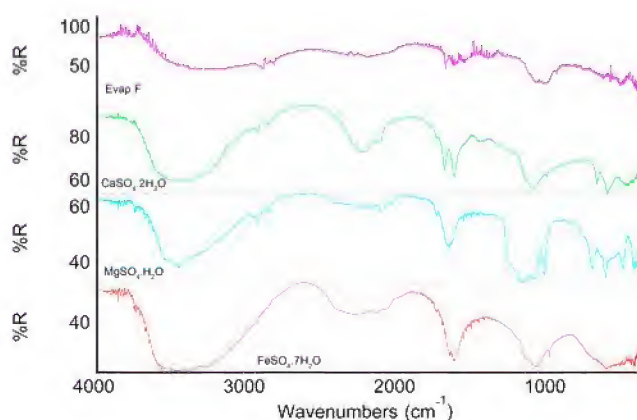


Figure 7. FTIR reflectance spectrum of evaporite formed by fast evaporation of Mars analog brine under simulated present-day conditions on Mars. Sample F has the diagnostic deep bands at 3000 and 3100 cm^{-1} of a CaSO_4 , probably kieserite, although more hydrated forms are also possible. Comparison with the ASU spectral library [Christensen *et al.*, 2000b] shows the presence of Ca and Mg sulfates. Spectra of gypsum, kieserite, and ferrous sulfate, taken with the same instrument under the same conditions are shown for comparison.

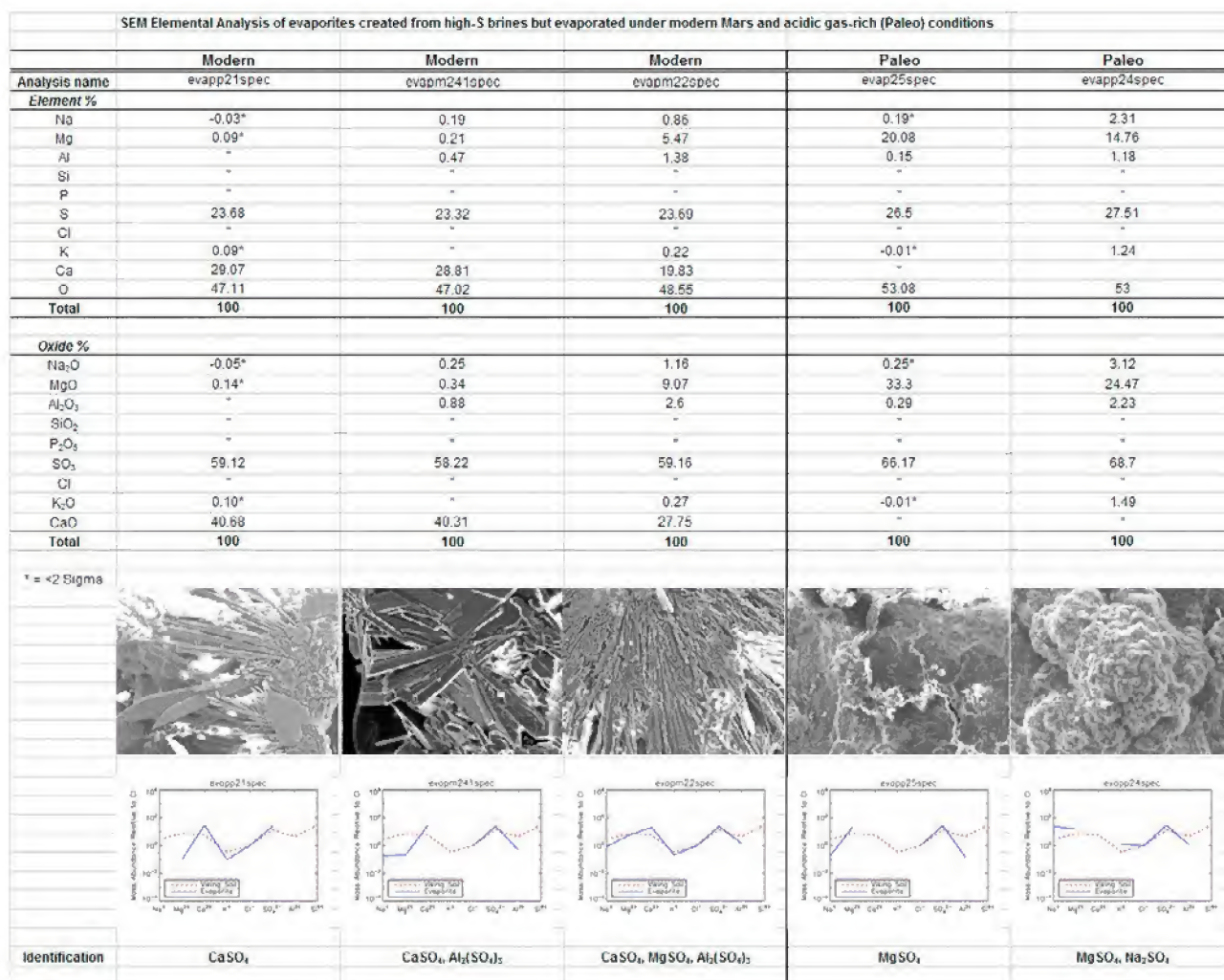


Figure 8. SEM elemental analysis of evaporites created from high S brines and evaporated under modern Mars (modern) and acidic gas-rich (paleo) conditions.

richer in S because of replenishment by SO₂ from the head-space gas. The lower pH of these waters encouraged the precipitation of MgSO₄ rather than CaSO₄, and the abundance of dissolved S was high enough that other cations, such as Al, Na, and K, also precipitated in minor amounts as sulfates. Mars analog brines that evaporated under present Mars conditions precipitated mostly CaSO₄, and smaller amounts of the minor sulfate phases. The fact that Ca sulfates are preferentially formed under present atmosphere is consistent with the “recent” formation process of the unique gypsum-rich dunes detected in Olympia Planitia proposed by *Fishbaugh et al.* [2007].

[32] Our experiments show that the relative abundance of minor sulfate phases can be diagnostic for the kind of atmosphere under which the evaporite formed. Specifically, Na₂SO₄ was associated with the precipitation of MgSO₄ under acidic Mars conditions and Al₂(SO₄)₃ was more prevalent in the CaSO₄ precipitates produced from the evaporation of the Mars analog brine under present Martian conditions.

[33] More experiments testing a wider range of chemistries and aqueous histories will be necessary to understand the

formation of salt mineralogies being revealed on Mars by TES, OMEGA, the MERs, and now CRISM.

8. Conclusions

[34] Using a specially built apparatus for simulating the chemical, pressure, and temperature conditions of present Mars, and a model for early Mars, we produced four varieties of evaporites. The chemical composition of the precursor brine was guided by previous laboratory work that focused on the production of a Mars analog brine from an SNC-derived mineralogy under a model paleo-Mars atmosphere with added volcanic gases [*Bullock and Moore, 2004*]. Evaporites were formed by fast (days) and slow evaporation (weeks), and under a gas simulated the present-day Mars atmosphere and a gas simulating the acidic paleo-Mars atmosphere.

[35] Infrared reflectance spectroscopy and SEM microprobe analyses revealed that salts precipitated from the evaporating brine under simulated present Mars conditions were chemically different from those formed under the acidic Mars atmosphere conditions. Electron probe and IR spectroscopy show that evaporites precipitating out of a simulated

present-day Martian brine consists mostly of calcium sulfates. Small amounts of magnesium and aluminum sulfates also comprised these precipitates.

[36] Similar analyses of evaporites that precipitate out of brines under a simulated acidic atmosphere show that they are mostly magnesium sulfates, although calcium sulfates are also formed in significant amounts. Smaller amounts of Na, Al, and K sulfates also precipitated under these conditions, with these minor phases being more abundant than in precipitates formed under present Mars conditions.

[37] These experiments suggest ways that relative cation abundances in Martian salt-bearing sediments can indicate the atmospheric and aqueous conditions under which they were formed. Mg sulfates dominate the sulfate chemistry of the Meridiani outcrop, but Ca, Fe, and K sulfates were also detected by Opportunity. The chemistry of the Meridiani outcrop sulfates more closely resembles the evaporites that we produce under simulated acidic paleo-Mars conditions, with small amounts SO₂, NO₂, and HCl gases present. We conclude that the salts that make up the Meridiani sediments were probably formed by the interaction of water and igneous rocks at a high water-to-rock ratio, followed by desiccation under an atmosphere rich in acidic volcanic volatiles. The formation of Ca sulfates on Mars was most likely due to the evaporation or freezing and sublimation of waters in equilibrium with an atmosphere much like the present one.

[38] **Acknowledgments.** The authors wish to thank Carrie Chavez and Clayton Woosley for their careful analytical work in the laboratory. Richard Quinn developed the synthetic brines recipe, for which we are grateful. This work was funded by a grant to J.M.M. from NASA's Planetary Geology and Geophysics Program (NNX07AE38A) and by NASA Mars Fundamental Research Program grants NNX07AR68G to M.A.B. and NNG04GE87G to H.E.N.

References

- Arvidson, R. E., F. P. Seelos IV, K. S. Deal, W. C. Koeppen, N. O. Snider, J. M. Kieniewicz, B. M. Hynek, M. T. Mellon, and J. B. Garvin (2003), Mantled and exhumed terrains in Terra Meridiani, Mars, *J. Geophys. Res.*, **108**(E12), 8073, doi:10.1029/2002JE001982.
- Arvidson, R. E., F. Poulet, J.-P. Bibring, M. Wolff, A. Gendrin, R. V. Morris, J. J. Freeman, Y. Langevin, N. Mangold, and G. Bellucci (2005), Spectral reflectance and morphologic correlations in eastern Terra Meridiani, Mars, *Science*, **307**, 1591–1594, doi:10.1126/science.1109509.
- Banin, A., F. X. Han, I. Kan, and A. Cicelsky (1997), Acidic volatiles and the Mars soil, *J. Geophys. Res.*, **102**, 13,341–13,356, doi:10.1029/97JE01160.
- Bibring, J.-P., Y. Langevin, A. Gendrin, B. Gondet, F. Poulet, M. Berthe, A. Soufflot, R. Arvidson, N. Mangold, J. Mustard, P. Drossart, and the OMEGA team (2005), Mars surface diversity as revealed by the OMEGA/Mars Express observations, *Science*, **307**, 1576–1581, doi:10.1126/science.1108806.
- Bibring, J.-P., et al. (2006), Global mineralogical and aqueous Mars history derived from OMEGA/Mars Express data, *Science*, **312**, 400–404, doi:10.1126/science.1122659.
- Bullock, M. A., and J. M. Moore (2004), Aqueous alteration of Mars-analog rocks under an acidic atmosphere, *Geophys. Res. Lett.*, **31**, L14701, doi:10.1029/2004GL019980.
- Bullock, M. A., and J. M. Moore (2007), Atmospheric conditions on early Mars and the missing layered carbonates, *Geophys. Res. Lett.*, **34**, L19201, doi:10.1029/2007GL030688.
- Bullock, M. A., J. M. Moore, and M. T. Mellon (2004), Laboratory simulations of Mars aqueous geochemistry, *Icarus*, **170**, 404–423, doi:10.1016/j.icarus.2004.03.016.
- Burt, D. M., L. P. Knauth, and K. H. Wohletz (2005), Origin of layered rocks, salts, and spherules at the opportunity landing site on Mars: No flowing or standing water evident or required, *Lunar Planet. Sci.*, XXXVI, Abstract 1527.
- Chevrier, V., P. Rochette, P. E. Mathe, and O. Grauby (2004), Weathering of iron-rich phases in simulated Martian atmospheres, *Geology*, **32**, 1033–1036, doi:10.1130/G21078.1.
- Christensen, P. R., and S. W. Ruff (2004), Formation of the hematite-bearing unit in Meridiani Planum: Evidence for deposition in standing water, *J. Geophys. Res.*, **109**, E08003, doi:10.1029/2003JE002233.
- Christensen, P. R., et al. (2000a), Detection of crystalline hematite mineralization on Mars by the Thermal Emission Spectrometer: Evidence for near-surface water, *J. Geophys. Res.*, **105**, 9623–9642, doi:10.1029/1999JE001093.
- Christensen, P. R., J. L. Bandfield, V. E. Hamilton, D. A. Howard, M. D. Lane, J. L. Piatek, S. W. Ruff, and W. L. Stefanov (2000b), A thermal emission spectral library of rock-forming minerals, *J. Geophys. Res.*, **105**, 9735–9739, doi:10.1029/1998JE000624.
- Clark, B. C., and D. C. Van Hart (1981), The salts of Mars, *Icarus*, **45**, 370–378, doi:10.1016/0019-1035(81)90041-5.
- Clark, B. C., A. K. Baird, H. J. Rose, K. Keil, A. J. Castro, W. C. Kelliher, C. D. Rowe, and P. H. Evans (1976), Inorganic analyses of Martian surface samples at the Viking landing sites, *Science*, **194**, 1283–1288, doi:10.1126/science.194.4271.1283.
- Clark, B. C., et al. (2005), Chemistry and mineralogy of outcrops at Meridiani Planum, *Earth Planet. Sci. Lett.*, **240**, 73–94, doi:10.1016/j.epsl.2005.09.040.
- Edgett, K. S., and M. C. Malin (2002), Martian sedimentary rock stratigraphy: Outcrops and interbedded craters of northwest Sinus Meridiani and southwest Arabia Terra, *Geophys. Res. Lett.*, **29**(24), 2179, doi:10.1029/2002GL016515.
- Edgett, K. S., and M. C. Malin (2005), The sedimentary rocks of Meridiani Planum, in context, *Lunar Planet. Sci.*, XXXVI, Abstract 1171.
- Fishbaugh, K. E., F. Poulet, V. Chevrier, Y. Langevin, and J.-P. Bibring (2007), On the origin of gypsum in the Mars north polar region, *J. Geophys. Res.*, **112**, E07002, doi:10.1029/2006JE002862.
- Gendrin, A., et al. (2005), Sulfates in Martian layered terrains: The OMEGA/Mars Express view, *Science*, **307**, 1587–1591, doi:10.1126/science.1109087.
- Glotch, T. D., and J. L. Bandfield (2006), Determination and interpretation of surface and atmospheric Miniature Thermal Emission Spectrometer spectral end-members at the Meridiani Planum landing site, *J. Geophys. Res.*, **111**, E12S06, doi:10.1029/2005JE002671.
- Griffes, J. L., R. E. Arvidson, F. Poulet, and A. Gendrin (2007), Geologic and spectral mapping of etched terrain deposits in northern Meridiani Planum, *J. Geophys. Res.*, **112**, E08S09, doi:10.1029/2006JE002811.
- Grotzinger, J. P., R. E. Arvidson, J. F. Bell III, W. Calvin, B. C. Clark, D. A. Fike, M. Golombek, R. Greeley, A. Haldemann, and K. E. Herkenhoff (2005), Stratigraphy and sedimentology of a dry to wet eolian depositional system, Burns formation, Meridiani Planum, Mars, *Earth Planet. Sci. Lett.*, **240**, 11–72, doi:10.1016/j.epsl.2005.09.039.
- Grotzinger, J., et al. (2006), Sedimentary textures formed by aqueous processes, *Erebus crater, Meridiani Planum, Mars, Geology*, **34**, 1085–1088, doi:10.1130/G22985A.1.
- Hynek, B. M. (2004), Implications for hydrologic processes on Mars from extensive bedrock outcrops throughout Terra Meridiani, *Nature*, **431**, 156–159, doi:10.1038/nature02902.
- Hynek, B. M., R. E. Arvidson, and R. J. Phillips (2002), Geologic setting and origin of Terra Meridiani hematite deposit on Mars, *J. Geophys. Res.*, **107**(E10), 5088, doi:10.1029/2002JE001891.
- Langevin, Y., F. Poulet, J.-P. Bibring, and B. Gondet (2005), Sulfates in the north polar region of Mars detected by OMEGA/Mars Express, *Science*, **307**, 1584–1586, doi:10.1126/science.1109091.
- Loizeau, D., et al. (2007), Phyllosilicates in the Mawrth Vallis region of Mars, *J. Geophys. Res.*, **112**, E08S08, doi:10.1029/2006JE002877.
- McLennan, S. M., J. F. Bell III, W. M. Calvin, P. R. Christensen, B. C. Clark, P. A. de Souza, J. Farmer, W. H. Farrand, D. A. Fike, and R. Gellert (2005), Provenance and diagenesis of the evaporite-bearing Burns formation, Meridiani Planum, Mars, *Earth Planet. Sci. Lett.*, **240**, 95–121, doi:10.1016/j.epsl.2005.09.041.
- McLennan, S. M., R. E. Arvidson, B. C. Clark, J. P. Grotzinger, B. L. Joliff, A. H. Knoll, S. W. Squyres, N. J. Tosca, and A. S. Team (2007), Geochemistry, mineralogy and diagenesis of the Burns formation at Meridiani Planum: Insights into the sedimentary rock cycle on Mars, in *Seventh International Conference on Mars, July 9–13, 2007, Pasadena CA* [CD-ROM], *LPI Contrib.*, **1353**, Abstract 3231.
- McSween, H. Y., and K. Keil (2000), Mixing relationships in the Martian regolith and the composition of globally homogeneous dust, *Geochim. Cosmochim. Acta*, **64**, 2155–2166, doi:10.1016/S0016-7037(99)00401-9.
- Moore, J. M. (2004), Mars: Blueberry fields for ever, *Nature*, **428**, 711–712, doi:10.1038/428711a.

- Murchie, S. L., et al. (2008), Geology of the Caloris Basin, Mercury: A view from Messenger, *Science*, *321*, 73–76, doi:10.1126/science.1159261.
- Newsom, H. E., and J. J. Hagerty (1997), Chemical components of the Martian soil: Melt degassing, hydrothermal alteration, and chondritic debris, *J. Geophys. Res.*, *102*, 19,345–19,355, doi:10.1029/97JE01687.
- Poulet, F., J. -P. Bibring, J. F. Mustard, A. Gendrin, N. Mangold, Y. Langevin, R. E. Arvidson, B. Gondet, C. Gomez, and the OMEGA team (2005), *Phyllosilicates on Mars and implications for early Martian climate*, *Nature*, *438*, 623–627, doi:10.1038/nature04274.
- Poulet, F., Y. Langevin, G. Boubin, D. Jouglet, J. P. Bibring, and B. Gondet (2008), Spectral variability of the Martian high latitude surfaces, *Geophys. Res. Lett.*, *35*, L20201, doi:10.1029/2008GL035450.
- Squyres, S. W., et al. (2004), In situ evidence for an ancient aqueous environment at Meridiani Planum, *Mars, Science*, *306*, 1709–1714, doi:10.1126/science.1104559.
- Tosca, N. J., and S. M. McLennan (2006), Experimental constraints on evaporation processes at Meridiani Planum, *Lunar Planet. Sci.*, *XXXVII*, Abstract 2260.
- Tosca, N. J., S. M. McLennan, B. C. Clark, J. P. Grotzinger, J. A. Hurowitz, A. H. Knoll, C. Schroder, and S. W. Squyres (2005), Geochemical modeling of evaporation processes on Mars: Insight from the sedimentary record at Meridiani Planum, *Earth Planet. Sci. Lett.*, *240*, 122–148, doi:10.1016/j.epsl.2005.09.042.
- Tosca, N. J., S. M. McLennan, M. D. Dyar, E. C. Sklute, and F. M. Michel (2008), Fe oxidation processes at Meridiani Planum and implications for secondary Fe mineralogy on Mars, *J. Geophys. Res.*, *113*, E05005, doi:10.1029/2007JE003019.
- Toulmin, P., A. K. Baird, B. C. Clark, K. Keil, H. J. Rose, R. P. Christian, P. H. Evans, and W. C. Kelliher (1977), Geochemical and mineralogical interpretation of the Viking inorganic chemical results, *J. Geophys. Res.*, *82*, 4625–4634, doi:10.1029/JS082i028p04625.
- Zent, A. P., and F. P. Fanale (1986), Possible Mars brines: Equilibrium and kinetic considerations, *Proc. Lunar Planet. Sci. Conf.*, *16th*, Part 2, *J. Geophys. Res.*, *91*, suppl., D439–D445, doi:10.1029/JB091iB04p0D439.
- Zent, A. P., F. P. Fanale, and L. E. Roth (1990), Possible Martian brines: Radar observations and models, *J. Geophys. Res.*, *95*(B9), 14,531–14,542, doi:10.1029/JB095iB09p14531.
- Zolotov, M. Y., and E. L. Shock (2005), Formation of jarosite-bearing deposits through aqueous oxidation of pyrite at Meridiani Planum, Mars, *Geophys. Res. Lett.*, *32*, L21203, doi:10.1029/2005GL024253.

M. A. Bullock, Department of Space Studies, Southwest Research Institute, 1050 Walnut St., Ste. 300, Boulder, CO 80302, USA. (bullock@boulder.swri.edu)

J. M. Moore, NASA Ames Research Center, M/S 245-3, Moffett Field, CA 94035, USA. (jeff.moore@nasa.gov)

M. Nelson and H. Newsom, Institute of Meteoritics, Department of Earth and Planetary Sciences, MSC03-2050, University of New Mexico, Albuquerque, NM 87131, USA. (mnelson@unm.edu; newsom@unm.edu)